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<b>(21) International Application Number:</b> PCT/US96/00963 <b>(22) International Filing Date:</b> 24 January 1996 (24.01.96)  <b>(30) Priority Data:</b> 08/473,444                      7 June 1995 (07.06.95)                      US  <b>(71) Applicant:</b> PT SUB, INC. [US/US]; 1031 Centre Road, Wilmington, DE 19805 (US).  <b>(72) Inventor:</b> TSAO, Jung, Hsien; 1444 Brookcliff Court, Marietta, GA 30062 (US).  <b>(74) Agents:</b> LEVIN, Gary, H. et al.; Woodcock Washburn Kurtz Mackiewicz & Norris, 46th floor, One Liberty Place, Philadelphia, PA 19103 (US).		<b>(81) Designated States:</b> AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> THIOL-CONTAINING PHOTSENSITIVE POLYMERIC FOAM COMPOSITIONS  <b>(57) Abstract</b>  This invention relates to thiol-containing photosensitive polymeric compositions and foam compositions that are formed by mechanically frothing the polymeric composition and curing the resulting froth with radiation to yield a foam composition. The invention also relates, <i>inter alia</i> , to laminates such as printing blankets and foam sheets comprising the thiol-containing polymeric foam compositions of the invention, and graphic art devices such as compressible printing plates comprising the same.		

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## THIOL-CONTAINING PHOTSENSITIVE POLYMERIC FOAM COMPOSITIONS

### FIELD OF THE INVENTION

This invention relates to thiol-containing photosensitive polymeric compositions and thiol-containing foam compositions that are formed by mechanically frothing a polymeric composition and curing the resulting froth with radiation to yield a foam composition. The invention also relates, *inter alia*, to laminates such as printing blankets and foam sheets comprising the thiol-containing polymeric foam compositions of the invention, and graphic art devices such as compressible printing plates comprising the same.

### BACKGROUND OF THE INVENTION

The use of foam in compressible printing blankets and other graphic art devices such as printing plates, engraver's gums, box die mounting boards, and drawsheets is well known in the art.

Compressible printing blankets offer printers an advantage over noncompressible printing blankets by eliminating the need for precise underpacking to achieve an acceptable amount of pressure between printing plate, printing blanket, and the paper or other material to be printed. These compressible printing blankets often use foam, normally a very thin layer, to keep the pressure relatively constant over a wide range of squeeze. The foam should have good compression set resistance, uniform compressibility, uniform gauge (so as to print uniformly), should be capable of being applied during the manufacture of

the blanket, and should be capable of being cured to a uniform gauge.

Foaming agents and blowing agents (*i.e.*, compounds capable of releasing gases such as carbon dioxide by decomposition, normally at high temperatures) have been used to produce foams in the past from polymer lattices and solutions of polymers in organic solvents. Such foams have been cured at high temperatures, over an extended period of time, using sulfur as a curative. However, foams prepared using these systems often did not possess the important properties of uniform compressibility, uniform gauge, and good compression set resistance. These deficiencies were likely caused by the high temperature operations of foaming, curing, and water or solvent removal all of which can result in nonuniform foam formation. Problems associated with foam formation are particularly acute when the operations are time consuming and result in a partial collapse of the foam before sufficient curing has occurred to maintain the foam structure and gauge. Nonuniform foams are poor candidates for use in graphic art devices as printing blankets or printing plates due, in part, to their nonuniform compressibility.

There are foams available in the art made from photosensitive polymeric materials that have the properties of uniform compressibility, uniform gauge, and good compression set resistance. Examples of such foam compositions are disclosed in U.S. Patent No. 4,771,078 entitled, "Method of Producing a Foam From a Radiation-Curable Composition" assigned to a common assignee hereof, the disclosure of which is herein incorporated by reference in its entirety. Foams such as those disclosed in U.S. Patent No. 4,771,078 can result in a relatively hard foam sheet, and thus, a composite printing plate or a printing blanket incorporating the foam can have limited compressibility. Also, it is sometimes desirable to use a thicker layer of foam to enhance the foam's cushioning capabilities, but when such thicker foams are made according

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to current techniques (i.e., see U.S. Patent Nos. 4,771,078, 4,767,793, and 4,528,777), the ultraviolet transmittance of the foam can become too low. It can then become difficult to make a composite printing plate because the lack of

5 radiation can hinder back exposure and proper adhesion between the foam and the photocurable material used as the printing face.

So, despite the advances in the art disclosed in patents such as U.S. Patent Nos. 4,771,078, 4,767,793, and  
10 4,582,777, there is still a need for softer foams that can be used at a thicker gauge and yet maintain good ultraviolet transmittance, as well as balance the composition's properties of hardness and toughness. The present invention addresses these needs among others by providing thiol-  
15 containing photosensitive polymeric compositions and foam compositions made therefrom that possess, *inter alia*, good compression set resistance and uniform compressibility, and are capable of being cured to uniform gauge.

#### SUMMARY OF THE INVENTION

20 This invention presents, *inter alia*, thiol-containing photosensitive polymeric foam compositions. The novel photosensitive polymeric foam compositions of the invention provide the basis for improved graphic art devices such as printing blankets, foam sheets, and compressible  
25 printing plates. The photosensitive polymeric foam compositions of the invention possess unique properties that make them good materials for use in laminates and graphic art devices such as printing blankets and printing plates.

For example, the polymeric foam compositions of  
30 the invention are softer than those currently used in the art, which, *inter alia*, provides better compressibility. Yet, the softness of the polymeric foam compositions of the invention does not compromise their property of toughness. It is believed that the thiol component present in the  
35 composition imparts a unique balance of softness and toughness that makes the compositions of the invention

excellent materials for incorporation into graphic art devices. The polymeric foam compositions of the invention also have the further quality of being highly transparent to ultraviolet light, even when used in graphic art devices at  
5 thicknesses greater than those currently used in the art. This property enables one to prepare a compressible printing plate that can be back exposed. The use of a thicker foam in such plates also has the added benefit of increased compressibility which, *inter alia*, prevents  
10 distortion of the print.

In accordance with the practice of the present invention, disclosed are thiol-containing photosensitive resin compositions comprising (a) 100 parts by weight of a urethane prepolymer comprising a plurality of diol segments  
15 linked through a urethane linkage and having an addition-polymerizable ethylenically unsaturated group at both terminal ends thereof, the plurality of diol segments being selected from the group consisting of polyester diols, polyether diols, and combinations thereof; (b) about 1 to 50  
20 parts by weight, relative to the 100 parts by weight of the urethane prepolymer (a), of a thiol component; (c) about 5 to 80 parts by weight, relative to the 100 parts by weight of the urethane prepolymer (a), of a reactive diluent; and  
(d) about 0.1 to about 5 parts by weight, relative to the  
25 100 parts by weight of the urethane prepolymer (a), of a photoinitiator and/or photosensitizer.

The thiol-containing photosensitive resin compositions may further comprise a plasticizer and/or surfactant, such resin compositions comprise about 1 to 15  
30 parts by weight, relative to the 100 parts by weight of the urethane prepolymer (a) of a plasticizer and about 0.1 to 5 parts by weight, relative to the 100 parts by weight of the urethane prepolymer (a) of a surfactant.

The invention is further directed to thiol-  
35 containing polymeric foam compositions made from the photosensitive resin compositions of the invention.

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In another aspect of the invention, articles incorporating the thiol-containing polymeric foam compositions of the invention are disclosed. In particular, laminates including, but not limited to, foam sheets and printing blankets are disclosed. The laminates incorporating the novel foam compositions of the invention have various uses including, but not limited to, being used on business forms and envelope printing presses to transfer ink from a printing plate to the paper, printing cushions, as packing blankets on newspaper offset presses, compressible printing blankets when the topcoat selected is ink receptive and solvent resistant, compressible packing blankets for flexographic printing plates, printing blankets for letterpress drawsheets, as a part of rubber stamps, and compressible offset printing blankets. See also U.S. Patent No. 4,771,078.

Also disclosed are graphic art devices including, but not limited to, compressible printing plates comprising the novel foam compositions of the invention. Uses of foam compositions in printing plates are disclosed, for example, in U.S. Patent No. 4,582,777, the disclosure of which is herein incorporated by reference in its entirety.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts an embodiment of a compressible printing plate comprising a layer of a foam composition of the invention. The photopolymer layer 1 is used to form a relief image on the facing of the plate. Immediately under layer 1 is the foam layer 3 which is attached to a film backing 7, in part, by a tie coat 5.

Figure 2 depicts another embodiment of a compressible printing plate comprising a layer of a foam composition of the invention. The photopolymer layer 2 is used to form a relief image on the facing of the plate. Immediately under the layer 2 is the foam layer 4 which is reinforced with a mesh reinforcing element 6, such as a

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fiber-glass coarse screen, rather than the combination of a tie coat and the film backing as shown in Figure 1.

#### DETAILED DESCRIPTION OF THE INVENTION

In the context of this invention, the terminology  
5 "graphic art devices" is used generally and is meant to include, without limitation, laminates, printing plates, and the like.

As used in this invention, the term "prepolymer" is meant to include adducts or reaction intermediates and  
10 includes oligomers. The term "oligomer" as used herein includes, but is not limited to, low molecular weight polymers having only a few monomeric units. Typical oligomers normally have molecular weights below 30,000, but such weights may range from 500 to 10,000; 5,000 to 20,000;  
15 or 1,000 to 15,000. The molecular weight may be determined using gel permeation chromatography using a styrene standard, which usually gives both the number average and the weight average of the composition of interest. As used herein, the term "diol" is used synonymously with the term  
20 oligomer and refers to, without limitation, polyols including, without limitation, polyethers, polyesters, or combinations thereof.

The terminology "polymer" and "resin" are used interchangeably and refer to the liquid-like composition  
25 that is the precursor to the foam compositions of the invention. In other words, it is the resin composition that is frothed and then cured to yield a foam composition of the invention.

The terminology "reactive diluent," as used  
30 herein, refers to a low viscosity monomer which is compatible with the prepolymers used herein and is used to lower the viscosity of the prepolymer to a manageable liquid state and also to take part in the radiation initiated polymerization or crosslinking. As used herein, the  
35 terminology "reactive functional group" or "functional" (when used in reference to an atom or compound) refers to a



portion of the compound that participates in a reaction including, without limitation, polymerization and/or crosslinking. In the context of this invention, the term "aliphatic" refers to any carbon-hydrogen containing compounds having either saturated or unsaturated bonds (alkanes, alkenes, alkynes), such compounds may be cyclic or acyclic, straight or branched chains, and may further be substituted with hetero atoms. The term "aromatic," as used herein, refers to any compounds that contains at least one benzene ring.

The term "photoinitiator," as used herein, refers to compounds that are effective in promoting free radical addition polymerization by generating reactive species, such as free radicals, by way of unimolecular scission resulting from photoexcitation. In the context of this invention, the term "photosensitizers" refers to compounds that are effective in promoting free radical addition polymerization through bimolecular photochemical reactions of the energy donor or transfer type or hydrogen abstraction type or by formation of a donor-acceptor complex with monomers or additives leading to ionic or radical species.

As used herein, a "plasticizer" is a compound added to a polymeric, prepolymeric, or oligomeric composition both to facilitate processing and to increase the flexibility and toughness of the final product. A "surfactant," as used herein, is a compound which reduces the surface tension of a liquid or which reduces the interfacial tension between two liquids or between a liquid and a solid and promotes the stability of froths.

In the context of this invention, the terminology "photosensitive" and "radiation curable" are used interchangeably. The terminology "radiation curable" means capable of being crosslinked and/or polymerized and/or copolymerized by exposure to radiation either inherently, (i.e., in the absence of photoinitiators and/or photosensitizers), or through the use of photoinitiators and/or photosensitizers. The term "radiation," as used herein, is

meant to exclude thermal radiation and low energy electromagnetic radiation in the microwave and radiowave regions but to include ionizing radiation such as gamma rays, x-rays, and subatomic charged particles when  
5 accelerated in a cyclotron or betatron. The language "radiation curing," as used herein, is intended to include photopolymerization, photocuring, and all forms of polymeric matrix (network) formation resulting from radiation including, but not limited to, covalent carbon to carbon  
10 crosslinkings, homopolymerization, copolymerization, branching, and grafting.

The term "photocurable," as used herein, denotes the capability of being cured by actinic type radiation (i.e., radiation in the visible and ultraviolet spectral  
15 regions). A "photopolymerizable composition," as that language is used herein, is one capable of being cured by actinic radiation and generally contains a photoinitiator and/or photosensitizer.

Radiation treatment of compositions to produce  
20 cured polymeric materials, as those claimed and disclosed herein, is well known in the art. For example, the prior art discloses the various forms of radiation which can be used, when photoinitiators and/or photosensitizers should be used, and what compositions may be cured and/or polymerized by the  
25 radiation (i.e., for example, reactive diluent/oligomer compositions). See, e.g., U.S. Patent Nos. 4,582,777; 4,771,078; 4,767,793; 4,816,315; and 4,415,615, the disclosures of which are herein incorporated by reference in their entirety.

30 The mechanical frothing of liquid compositions to produce polymeric foams is also well known in the art. See, e.g., U.S. Patent Nos. 4,582,777; 4,771,078; 4,767,793; and 4,415,615, the disclosures of which are herein incorporated by reference in their entirety.

35 The present invention involves the discovery that by using well known mechanical frothing techniques with well known radiation techniques, foams having a highly uniform

compressibility across their entire surfaces and good resistance to compression set can be prepared from the thiol-containing resin compositions disclosed herein. Both of these properties are extremely important in foam layers used in graphic arts devices. The thiol-containing polymeric foam compositions of the invention are an improvement over the currently available foams used in graphic art devices because they are softer, thus providing better compressibility, but retaining the required property of toughness. It is believed that the thiol component imparts a unique balance of softness and toughness to the compositions that make them excellent materials for incorporation into graphic art devices such as printing blankets. The thiol-containing polymeric foam compositions of the invention also exhibit a high level of ultraviolet transmittance, even at thicknesses greater than those presently used in graphic art devices. This enables one to generate foams with high compressibility which can be back-exposed, making these foams ideal candidates for use in graphic art devices such as composite printing plates.

The foam compositions of the present invention generally have the following characteristics.

The voids (bubbles) resulting from the frothing technique are essentially spherical in shape and are empty (i.e., do not contain foreign matter such as hollow microspheres, microballoons, frangible bubbles, the byproducts of chemical blowing agents, remnants thereof).

Some prior art foams are prepared by compounding a thin layer of polymer with salt and then extracting the salt with water to form voids. This salt extraction process forms voids with an irregular nonspherical, non-elliptical shape which have a greater tendency to merge into one another, thereby creating void networks. The foam of the present invention does not have irregularly shaped voids and such networks. Rather the voids in the foam of the present invention, as previously mentioned herein, are generally essentially spherical.

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Some foams require the presence of microballoons, cork, ground sponge rubber, microspheres, or frangible bubbles which either remain intact during the use of the foam or collapse or fracture during the use of the foam, the  
5 remnants thereof remaining within the voids. The voids in the foam of the present invention are empty (i.e., contain no such structures or remnants thereof).

The foam compositions of the present invention are generally closed cell foams (i.e., normally at least 80% of  
10 the void volume does not interact to form networks or pores).

The foam layer is generally essentially skin-free. This differs from some prior art foams where either or both of the upper and lower portions of the foam layer have a  
15 much lower concentration of voids (i.e., a lower void to solid ratio than the middle portion of the foam layer), either intentionally or unintentionally, in essence forming a relatively nonfoamed, skin layer. Where the foam layer can very thin, for example in printing blankets, the  
20 formation of a dense layer, essentially free of voids, within the foam layer, can seriously reduce the lower density portion of the foam. For example, where a foam layer is 60 mils thick and possesses top and bottom "skins" that are essentially non-foamed, and each 20 mils thick, the  
25 foamed portion in the center of the layer would only be 20 mils thick. In the skin-free foam of the present invention, essentially the entire 60 mils of thickness would be foamed. This not only provides increased compressibility, but provides the advantages that, should a variation in the  
30 gauge of the foam portion occur (for example by applying the foam layer by spreading, prior to curing or during curing), the variation in compressibility over the foam would be less than that for "skinned" foams.

Generally, radiation-curable compositions, such as  
35 those disclosed herein, can be obtained by mixing a polymer with a reactive diluent that is sufficiently miscible with the polymer to create a composition with a viscosity

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suitable for applying to a substrate and/or for foaming. As an alternative, a solid composition can be heated to a molten liquid state to provide a suitable viscosity. The radiation-curable compositions of the present invention should have a liquid consistency to permit mechanical frothing. If the liquid consistency can be obtained by heating a composition, such heating is permissible.

The resin and foam compositions of the invention generally comprise polyurethanes. Generally, polyurethanes are synthesized by reacting a diol with a diisocyanate. Diisocyanates suitable for practicing the invention include, but are not limited to, aliphatic or aromatic diisocyanates, with aliphatic isocyanate compounds being preferred. Diols or oligomers suitable for synthesizing the polyurethane prepolymers of the invention include, but are not limited to, polyethers, polyesters, or combinations thereof, with polyethers being preferred.

A preferred polyurethane prepolymer of the invention may be synthesized by reacting a diol, with a compound having at least two isocyanate groups, and a compound containing at least one functional hydrogen atom and at least one ethylenically unsaturated double bond. For example, a preferred prepolymer may be synthesized by mixing polytetramethyleneglycol and ethylene-oxide-propyleneoxide block polyetherdiol having about 30% by weight of ethylene oxide terminal units with dicyclohexylmethane diisocyanate to form a polyether urethane terminated with isocyanate groups. At least one compound selected from the group consisting of hydroxy ethylacrylate and hydroxy ethylmethacrylate is added to yield a prepolymer. The molecular weight of the prepolymer may be between about 700 to 30,000; more preferably it may be between about 5000 to 20,000, and most preferably it may be between about 1,000 to 15,000.

A preferred resin composition of the invention may then be synthesized, for example, by adding hydroxy ethylmethacrylate and polypropylene glycol monomethacrylate, a

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photoinitiator, such as hydroxy-2-methyl-1-phenylpropan-1-one, and a thiol-containing compound such as trimethylol propane tris-( $\beta$ -mercaptopropionate) to the above prepolymer. The Brookfield viscosity of the polymeric composition,  
5 measured at room temperature, generally may be between about 10,000 cps to 50,000.

The levels of the components which can be incorporated into the resin compositions of this invention, based on parts by weight per 100 parts by weight of the  
10 prepolymer are: preferably between about 5 to about 80 parts, more preferably between about 15 to about 55 parts of the reactive diluent; preferably between about 1 to about 50 parts, more preferably between about 3 to about 15 parts of the thiol component; preferably between about 0.1 to about 5  
15 parts, more preferably about 0.3 to about 2 parts of photosensitizer and/or photoinitiator; between about 1 to about 15 parts, preferably between about 5 to about 10 parts, and more preferably between about 1 to about 8 parts of a plasticizer; and between about 0.1 to about 5 parts,  
20 preferably between about 0.5 to about 2, and more preferably between about 0.5 to about 1.5 parts of the surfactant.

Other materials can be included in the composition, without detracting from the spirit of the invention, such as antioxidants, inhibitors, flame-retardant  
25 agents, tackifiers, and the like, the criteria being that the materials do not significantly impede the polymerization of the composition, nor prevent the transmission of radiation.

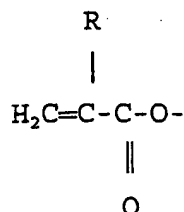
The prepolymers of the present invention may be  
30 reactive or non-reactive. Reactive oligomers or prepolymers include those that are capable of forming a free radical by exposure to radiation in the presence, if necessary, of a photoinitiator and/or photosensitizer, and normally contain unsaturation. It is to be understood that oligomers can  
35 include those materials which can be cured by exposure to radiation by other than a free radical mechanism (*i.e.*, epoxides, which are radiation cured by means of

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photolytically generated cationic catalysts). It is preferred that the oligomers used in the foam compositions of the invention be reactive because such oligomers take part in the polymerization or crosslinking reaction which is initiated by radiation as opposed to the non-reactive oligomers which are incorporated within the network of the polymerized reactive diluent.

If the radiation-curable composition is prepared from an oligomer and the viscosity of the oligomer is sufficiently low to be a liquid at room temperature or with some heating, it may be used with or without a reactive diluent as part of the radiation-curable composition. If no reactive diluent is used, then the oligomer must itself be reactive so as to form a polymer matrix during the radiation step. That is, the oligomer must contain reactive sites such as unsaturation in the form of carbon to carbon double bonds and/or epoxide groups which are activated by radiation, and if necessary, in the presence of a photoinitiator and/or a photosensitizer, to result in free radical and/or cationic cures. If a reactive diluent is used, the oligomer can be reactive or nonreactive. If the oligomer is nonreactive, then the reactive diluent is preferably multifunctional so as to form a polymer network.

Typical reactive prepolymers suitable for practicing the invention include, but are not limited to, those having acrylic or methacrylic acid ester groups in their backbone conforming to the following structural formula wherein R is selected from the group consisting of hydrogen and methyl.



Polyurethane prepolymers within the scope of this invention include, but are not limited to, aliphatic or aromatic urethane acrylate oligomers; acrylated epoxy urethanes; acrylated polyether urethanes; and acrylated polyester-polyether urethanes. It is preferred that the polyurethane oligomer be a polyether; more preferably, the oligomer is an aliphatic polyether urethane acrylate oligomer. Urethane prepolymers comprising the above functionality will be known to those skilled in the art and may be used without departing from the spirit of the invention. In certain preferred embodiments, the prepolymer will comprise two polyol monomeric units and three isocyanate moieties, with the two polyol units internally interrupted by an isocyanate group.

A reactive diluent is a low viscosity monomer which is compatible with the prepolymer and is used to lower the viscosity of the oligomer to a manageable liquid state and also to take part in the radiation initiated polymerization or crosslinking. Reactive diluents can be multifunctional monomers or monofunctional monomers. Typical multifunctional monomers are the di- and triacrylates and methacrylates, and combinations thereof. Typical monofunctional monomers are the alkyl-acrylates, aryl-acrylates, alkoxyalkyl-acrylates and methacrylates, and combinations thereof. It is preferred that the reactive diluent comprise at least one multifunctional monomer, preferably the reactive functional group is hydroxyl.

Reactive diluents are homopolymerizable, compatible, and polymerizable with the oligomer when the oligomer is reactive. The reactive diluents not only function to adjust (reduce) the viscosity of the composition, but also affect the cure rate as well as the properties of the cured foam compositions of the invention.

Reactive diluents suitable for use in the present invention include, but are not limited to, styrene; vinyl toluene;  $\alpha$ -methyl styrene; methyl acrylate; methyl methacrylate; propyl acrylate; butyl acrylate; 2-ethylhexyl



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acrylate; cyclohexyl acrylate; isodecyl acrylate; vinyl acetate; 2-phenoxy acrylate; glycidyl methacrylate; tetrahydrofuryl methacrylate; caprolactone acrylate; 1,6-hexanediol diacrylate; pentaerythritol triacrylate;

5 trimethylol propane triacrylate; aryloxyalkyl acrylates and methacrylates; alkoxyalkyl acrylates and methacrylates such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate; N-vinyl pyrrolidone; polypropylene glycol monomethacrylate. Particularly preferred reactive diluents

10 are hydroxy ethyl acrylate, hydroxy ethyl methacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, tripropylene glycol diacrylate, tripropylene glycol dimethacrylate, tetra hydrofuryl methacrylate, isocyanate methacrylate, tetra ethyleneglycol

15 dimethacrylate, 1,6-hexane diol dimethacrylate, pentaerythritol-tetramethacrylate, and combinations thereof. Particularly preferred reactive diluents include hydroxyethyl methacrylate, diethylene glycol dimethacrylate, and polypropylene glycol monomethacrylate. Other reactive

20 diluents known to those skilled in the art may be used without departing from the spirit of the invention.

Thiol-containing compounds suitable for practicing this invention should have more than one reactive SH functional group, and may be aliphatic or aromatic

25 compounds. Preferably the thiol compound has at least two, three, or four functional groups. Preferred thiol-containing compounds include, but are not limited to, trimethylolpropane tris-( $\beta$ -mercaptopropionate) and pentaerythritol tetrakis ( $\beta$ -mercaptopropionate), with

30 trimethylolpropane tris-( $\beta$ -mercaptopropionate) being a preferred one. Other thiol-containing compounds known to those skilled in the art may be used without departing from the spirit of the invention.

Photoinitiators and/or photosensitizers suitable

35 for use in the present invention include, but are not limited to, 2,2-dimethoxy-2-phenylacetophenone; 1-hydroxycyclohexyl phenyl ketone; 2-hydroxy-2-methyl-1-

phenylpropan-1-one; benzophenone; benzoin; acetophenone; benzoin methyl ether; Michler's ketone; xanthone; propiophenone; fluorenone; carbazole; 2-, 3-, or 4-methylacetophenones; chlorothioxanthenes; 2-acetyl-4-methylphenyl acetate; and 2,2-dimethoxy-2-phenylacetophenone. A preferred photoinitiator is 2,2-dimethoxy-2-phenylacetophenone, a more preferred photoinitiator is 1-hydroxycyclohexyl phenyl ketone, and an even more preferred photoinitiator is 2-hydroxy-2-methyl-1-phenylpropan-1-one.

10 Other photoinitiators/photosensitizers known to those skilled in the art may be used without departing from the spirit of the invention.

The thiol-containing photosensitive polymeric resin compositions of the invention may further comprise a plasticizer and/or surfactant.

Plasticizers are used to retain compression and permanent set resistance properties and/or to make a softer foam. Plasticizers suitable for use in the present invention include, but are not limited to, halogenated organics, tri-aryl phosphates, carboxylic acid esters of organic alcohols, phosphate esters of organic alcohols. A preferred plasticizer is dioctylphthalate, a more preferred plasticizer is dipropylene glycol dibenzoate, and an even more preferred one is tri-aryl phosphate. Other plasticizers known to those skilled in the art may be used without departing from the spirit of the invention.

Surfactants are used to enhance the frothing as well as to stabilize the froth prior to and during radiation curing. Surfactants suitable for use in the present invention include, but are not limited to, alkylaryl polyether alcohols, dioctyl sodium sulfosuccinate, silicone fluids, and amide derivatives of aliphatic alcohols. Preferred surfactants are ethoxylated-propoxylated block copolymers, a more preferred surfactant is lauryl monoethanolamide, and an even more preferred surfactants are fatty diethanolamides. Other surfactants known to those

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skilled in the art may be used without departing from the spirit of the invention.

The photosensitive polymeric resin compositions disclosed herein may be frothed and treated with radiation to yield the novel thiol-containing foam compositions of the invention. As previously stated, the methods of making polymeric radiation curable compositions are known in the art. In general, other than as otherwise described herein, the conventional, well known techniques of mechanical frothing and radiation curing may be used to prepare the foams of the present invention.

For example, the resin (i.e., comprising, for example, a prepolymer, reactive diluent, photoinitiator and/or photosensitizer) is then frothed by using any one of a number of commercially available high-shear mixers into which is metered the radiation-curable composition and the air or inert gas such as nitrogen. The ratio of gas to liquid is adjusted to produce a foam having the desired void volume and compressibility as well as physical properties. Generally, the gas will represent from 10% to 90% by volume of the cured foam, preferably 15% to 65%, and more preferably between about 20% to 45%.

Representative equipment and techniques used in mechanical frothing are blenders; homogenizers such as colloid mills; mechanical frothing machines such as those sold by the Oakes Machine Corporation and Ease, Inc., which continuously inject a gas into a liquid and provide high agitation and dispersion, wire whips, such as Hobart mixers with planetary gears. Any other frothing equipment known to those skilled in the art may be used without detracting from the spirit of the invention.

The froth is normally distributed on a releasable sheet, on a substrate, or between two substrates (one or both of which will allow the passage of radiation), and the froth is then exposed to radiation until cured. A process for making a foam composition is set forth in the Examples and is further illustrated in U.S. Patent No. 4,771,078, the

disclosure of which is incorporated herein by reference in its entirety.

Representative of prior art, which reveals radiation curing techniques and radiation-curable compositions are U.S. Pat. Nos. 3,560,237; 3,535,193; 3,637,419; 3,700,541; 3,700,574; 3,715,293; 3,719,638; 3,891,523; 3,899,611; 4,038,350; 4,112,017; 4,376,800; 4,387,012; 4,483,951; 4,057,188; and Great Britain Patent Number 1,304,112.

10           There are four main sources of radiant energy: gamma rays, high energy electrons, neutrons, and actinic. Each of these sources has its respective advantages and disadvantages. The use of radiant energy to cure polymers is of fairly recent origin, and it is only in the last  
15 several years that the two most commercially attractive sources, actinic and electron beam, have been developed for use in industry. The apparatus or equipment necessary for generating the radiation is not the subject of this invention, and any source or apparatus capable of generating  
20 the required intensity of radiation known to persons of ordinary skill in the art can be used without departing from the spirit of the invention. A process for curing polymeric foam compositions of the invention is further described in U.S. Patent No. 4,771,078, the disclosure of which is  
25 incorporated herein by reference in its entirety.

          Generally, when actinic radiation is used to cure a photosensitive composition, the radiation-curable composition should contain reactive carbon to carbon double bonds (i.e., unsaturation, and photoinitiators and/or  
30 photosensitizers should be used). However, when a higher energy radiation, such as electron beam, is used, the unsaturation and photoinitiators/photosensitizer requirements are diminished. Overall, simple experimentation, coupled with prior art disclosures will  
35 permit persons of ordinary skill in the art to select the proper radiation parameters for the particular result desired.

Due to the short time required to completely cure the radiation-curable polymer composition, usually from about 0.5 seconds to about 60 seconds, preferably 1 to 15 seconds, if commercially available high intensity actinic radiation or high energy electron beam radiation sources are used, additional stages can be constructed to add further layers to the laminates.

It is to be understood that the state of cure can be varied by controlling the exposure time, the quantity of radiation, the distance from the source of radiation to the composition and the rate at which the composition is passed by the radiation source. Various states of cure can be utilized to provide any properties to the polymer which would make it more conducive to downstream processing. Any of these variations may be done without detracting from the spirit of the invention.

It should be noted that the frothed material need not be completely cured by radiation to benefit by the practice of the present invention. Rather it is sufficient that it be cured to a degree sufficient to cause the foam to maintain its structure indefinitely (i.e., to avoid the collapse of a significant portion of the frothed material and to maintain the gauge).

Sometimes it is actually beneficial to only partially cure the radiation-curable composition, for example when it is desirable that the surface of the foamed composition remain tacky for purposes of adhesion to a layer of material to be applied thereto subsequently in preparing a laminate. Completion of the cure can then follow.

The resulting cured thiol-containing polymeric foam compositions of the invention are a matrix (i.e., polymer network). Generally, the network is comprised of the polyurethane prepolymer, the reactive diluent, photoinitiator/photosensitizer, and the thiol component.

The cured polymeric foam composition of the invention may be laid out in sheets and may have a thickness of between about 10 to about 150 mils, more preferably

between about 20 to about 120 mils, and more preferably between about 40 to about 100 mils. The particular thickness of the foam used can depend on the application (i.e., whether the foam is used in a printing blanket or a printing plate).

The cured polymeric foam composition should preferably have a density between about 0.3 to about 1.0 g/cm<sup>3</sup>, more preferably between about 0.4 to about 0.9 g/cm<sup>3</sup>, and most preferably between about 0.6 to about 0.9 g/cm<sup>3</sup>. The density of the foamed composition may be determined using ASTM techniques, but other methods known to those skilled in the art can be used without departing from the spirit of the invention.

The cured polymeric foam composition should preferably have a resilience between about 25 to about 75%, more preferably between about 30 to about 50%, and most preferably between about 25 to about 45%. The resilience of the cured foam composition is generally determined using ASTM techniques, but other methods may be used without departing from the spirit of the invention.

The ultraviolet transmittance of the cured polymeric foam composition should preferably be between about 10% to about 30%, more preferably between about 30% to about 40%, and most preferably between about 40% to about 50%. Ultraviolet transmittance is generally determined by measuring the intensity of a light beam and then measuring the intensity of the same light beam with a piece of the cured foam placed in its path; the percent transmittance is then calculated based on the measured values. Other methods known to those skilled in the art may be used without departing from the spirit of the invention.

A preferred cured foam composition of the invention will have a thickness between about 40 to about 100 mils, a resilience between about 25 to about 50%, and an ultraviolet transmittance between about 10 to about 40%.

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In another aspect of the invention, articles incorporating the thiol-containing photosensitive polymeric foam compositions of the invention are disclosed. In particular, laminates including, but not limited to, foam sheets and printing blankets are disclosed. For example, a  
5 laminate can be formed using the foam of the invention sandwiched between two layers of fabric, without the use of additionally adhesives (i.e., tie coat) to adhere the foam to the fabric. The foam is its own fabric adhesive.

10 Fabrics useful for practicing the invention include, but are not limited to, cotton, nylon, polyester, aramid, rayon, acrylics, and the like. These fabrics are also suitable for use as backings for printing plates as disclosed herein. Depending on the type of fabric (i.e.,  
15 its weave, type of material, dip composition, etc.), greater or lesser amounts (intensities) of actinic radiation will be necessary for a proper degree of cure. Also where actinic radiation is used, the substrate should have a light color (i.e., not so dark as to absorb large amounts of the actinic  
20 radiation and thereby inhibit the curing of the composition).

The laminates incorporating the novel foam compositions of the invention have various uses including, but not limited to, being used on business forms and  
25 envelope printing presses to transfer ink from a printing plate to the paper, as packing blankets on newspaper offset presses, compressible printing blankets when the topcoat selected is ink receptive and solvent resistant, compressible packing blankets for flexographic printing  
30 plates, printing blankets for letterpress drawsheets, rubber stamps, and compressible offset printing blankets. See, e.g., U.S. Patent No. 4,771,078.

Also disclosed are graphic art devices including, but not limited to, printing plates comprising the novel  
35 compositions of the invention. See, e.g., U.S. Patent No. 4,582,777, the disclosure of which is incorporated by reference in its entirety.

For example, a printing plate comprising a foam composition of the invention may comprise a photopolymer layer having a thickness between about 150 to about 215 mils; a layer of a foam composition of the invention having a thickness of between about 35 to about 100 mils; a very thin layer of a tie coat (adhesive) having a thickness between about 0.1 to about 0.7 mils, preferably about 0.6 mils, and more preferably about 0.5 mils; and a film layer such as polyester having a thickness of between about 4 to about 10 mils. An example of such a compressible printing plate is depicted in Figure 1. An alternative printing plate within the scope of this invention comprises a mesh reinforcement such as a fiber glass screen in place of the film; this mesh coat has a thickness of between about 1 to about 20 mils, preferably between about 4 to about 20 mils, and most preferably about 10 to about 18 mils. Any mesh reinforcement elements known to those skilled in the art may be used without departing from the spirit of the invention. An example of such a printing plate is depicted in Figure 2.

In certain embodiments of the invention, when the foam composition is used in a printing plate it will preferably have a thickness of between about 40 to 100 mils, a density between about 0.6 to about 0.9 g/cm<sup>3</sup>, a resilience of between about 25 to about 50%, and an ultraviolet transmittance of between about 10% to about 40%.

The following examples are illustrative of the invention claimed and disclosed herein and are intended only to be used for illustrative purposes and are in no way intended to limit the invention.

### 30 EXAMPLES

#### EXAMPLE 1

##### Preparation of photosensitive polymeric composition

In a resin kettle 680 parts of polytetramethylene glycol (Mn = ~2000) and 705 parts of an ethylene oxide-polypropylene oxide block polyether diol (Mn = ~3000, and about 30% by weight of ethylene oxide terminal units) were



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mixed with 230 parts of the dicyclohexylmethane diisocyanate (Desmodur W by Miles). With the addition of 0.2 parts of stannous octoate, the mixture was allowed to heat for 2-3 hours at 75°C to form a polyurethane terminated with

5 isocyanate groups. Thereafter, 57 parts of hydroxyethyl acrylate, 1.4 parts of 2,6-di-t-butyl-4-methylphenol, and 0.2 parts of stannous octoate were added to the kettle and the heating was continued for about 2 hours at 75°C. This step was followed by the addition of 23 parts of

10 hydroxyethyl methacrylate. The heating of the mixture was continued for another 2-3 hours until the isocyanate groups were substantially consumed, as determined by the diminishing 2260  $\text{cm}^{-1}$  absorption peak on the IR spectrum. The resulting prepolymer had a Brookfield viscosity of

15 45,000-47,000 cps as measured at 60°C.

To 100 parts of the above prepolymer was added 11.5 parts of hydroxyethyl methacrylate, 22.5 parts of polypropylene glycol monomethacrylate, 11.3 parts of diethyleneglycol dimethacrylate, 0.45 parts of Darocur 1173

20 (2-hydroxy-2-methyl-1-phenylpropan-1-one, supplied by Ciba Geigy), and 4.4 parts of trimethylol propane tris-( $\beta$ -mercaptopropionate) (thiol supplied by Evan Chemical) to obtain a photosensitive polymeric composition with a Brookfield viscosity of 37,500 cps measured at 23°C.

## 25 Example 2

**Preparation of a foam sheet with a polyester backing for use as printing cushion or backing for a flexible printing plate**

The photosensitive polymeric composition of Example 1 was frothed on an Oakes™ mixer using nitrogen as

30 the frothing gas at such a level as to give about 20 to 30% volume percent of gas based on the composition. The froth, which had the consistency of shaving cream, was then fed into the nip of a doctor over a roll coater between two pieces of transparent, biaxially-orientated polyethylene

35 tetraphthalate films through a spreading means at a speed of 3 yards/minute to set the gauge, then exposed to ultraviolet

radiation using a combination of bank of fluorescent black light bulbs (90% emission at 300-400 nm) and medium pressure mercury vapor lamps to cure the foam sheet.

When one side of the polyethylene tetraphthalate  
5 film is coated with a thin layer of vinyl tie coat that forms good bonding with the polymer, a foam sheet with a permanent polyester backing support is then produced.

### Example 3

Preparation of a foam sheet with an embedded mesh component  
10 for support for use in flexible printing plates

The same foaming procedure as used in Example 2 was used except that a reinforcing fiber-glass coarse screen was fed with the froth into the coating head and between two polyester sheets. The resulting foam sheet produced had the  
15 embedded reinforcing screen instead of the polyester backing. By adjusting the nip gap on the coater, two gauges (40 mils and 63 mils) of foam sheet were produced. The 40 mils thus obtained had a resilience of about 31%, a density of about 0.88 g/cm<sup>3</sup>, an ultraviolet transmittance of about  
20 30%. The 63 mils thus obtained had a resilience of about 35%, density of about 0.88 g/cm<sup>3</sup>, and an ultraviolet transmittance of about 20%.

### Example 4

Lab foaming of the composition described in Example 1

25 The photosensitive polymeric composition of Example 1 was frothed in air by vigorous stirring with a kitchen blender to a creamy mass of about 0.55 g/cm<sup>3</sup> density. It was then coated between two plastic films and then cured under ultraviolet lights. After peeling off the two plastic  
30 films, a soft and tough foam sheet resulted having a thickness of about 35 mils, a resilience of about 34%, a density of about 0.62 g/cm<sup>3</sup>, and an ultraviolet transmittance of about 23%.

**Example 5****Preparation of photosensitive polymeric composition**

In a resin kettle 1550 parts of an ethylene oxide-propylene oxide block polyether diol ( $M_n = \sim 3000$ , and about 5 30% by weight of ethylene oxide terminal units) was mixed with 200 parts of dicyclohexylmethane diisocyanate (Desmodur W supplied by Miles). With the addition of 0.15 parts of stannous octoate the mixture was allowed to heat for 2-3 hours at 75°C to form a polyurethane terminated with 10 isocyanate groups. Thereafter 48 parts of hydroxyethyl acrylate, 2 parts of 2,6-di-t-butyl-4-methylphenol, and 0.3 parts of stannous octoate were added and the heating was continued for 2 hours at 70-75°C, followed by the addition of 20 parts of hydroxymethacrylate. The heating of the 15 mixture was then continued for another 2-3 hours until the isocyanate groups were substantially consumed, as determined by the diminishing of  $2260\text{ cm}^{-1}$  absorption peak on the IR spectrum. The prepolymer thus obtained had a Brookfield viscosity of 18,000 cps as measured at 60°C.

20 To 100 parts of the so obtained prepolymer were mixed 15.2 parts of hydroxyethyl methacrylate, 27.4 parts of polypropylene glycol monomethacrylate, 11 parts of diethyleneglycol dimethacrylate, 0.45 parts of Darocur 1173 (2-hydroxy-2-methyl-1-phenylpropan-1-one, supplied by Ciba 25 Geigy), and 4.7 parts of trimethylolpropane tris-( $\beta$ -mercaptopropionate) (supplied by Evans Chemical) to obtain a photosensitive resin composition with a Brookfield viscosity of 16,000 cps measured at 23° C.

**Example 6****30 Preparation of a foam sheet with a polyester backing for use in compressible printing plate**

The photosensitive polymeric composition of Example 5 was frothed in air by vigorous stirring with a kitchen blender to a creamy mass with a density of 0.58 35 g/cm<sup>3</sup>, coated between plastic films, and then cured by ultraviolet radiation to provide a very flexible, and tough

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foam sheet after peeling off the plastic film. The foam sheet was about 39 mils (1 mm) thick, had a density of about 0.67 g/cm<sup>3</sup>, a resilience of about 29%, and a capability of transmitting about 33% of ultraviolet light.

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## WHAT IS CLAIMED IS:

1. A photosensitive resin composition comprising:
  - a) 100 parts by weight of a urethane prepolymer comprising a plurality of diol segments linked through a urethane linkage and having an addition-polymerizable ethylenically unsaturated group at both terminal ends thereof, said plurality of said diol segments being selected from the group consisting of polyester diols, polyether diols, and combinations thereof;
  - b) about 1 to 50 parts by weight, relative to the 100 parts by weight of the said urethane prepolymer (a), of a thiol component;
  - c) about 5 to 80 parts by weight, relative to the 100 parts by weight of the said urethane prepolymer (a), of a reactive diluent; and
  - d) about 0.1 to about 5 parts by weight, relative to the 100 parts by weight of said urethane prepolymer (a), of a photoinitiator and/or photosensitizer.
2. The composition of claim 1 wherein said reactive diluent is an ethylenically unsaturated monomeric compound selected from the group consisting of diacrylates, triacrylates, methacrylates, dimethacrylates, trimethacrylates, aryl acrylates, alkoxyalkyl acrylates, alkoxyalkyl methacrylates, alkyl methacrylates, styrene, vinyl toluene,  $\alpha$ -methyl styrene, alkyl acrylates, cycloalkyl acrylates, cycloalkyl methacrylates, vinyl acetates, phenoxy acrylates, phenoxy methacrylates, polyol acrylates, polyol methacrylates, vinyl pyrrolidones, and combinations thereof.
3. The compound of claim 1 further comprising about 1 to 15 parts by weight, relative to the 100 parts by weight of the urethane prepolymer (a) of a plasticizer and about 0.1 to 5 parts by weight, relative to the 100 parts by weight of the urethane prepolymer (a) of a surfactant.

4. A composition of claim 1 wherein said thiol component is selected from the group consisting of trimethylolpropane tris-( $\beta$ -mercaptopropionate) and pentaerythritol tetrakis ( $\beta$ -mercaptopropionate).

5 5. A composition of claim 1 wherein said urethane prepolymer is selected from the group consisting of an aliphatic and aromatic urethane acrylate oligomers, acrylated epoxy urethanes, acrylated polyether urethanes, and acrylated polyester-polyether urethanes.

10 6. A composition of claim 5 wherein said urethane prepolymer is an aliphatic polyether urethane acrylate.

15 7. A composition of claim 1 which comprises about 3 parts to about 15 parts of said thiol component, about 15 to about 55 parts of said reactive diluent, and about 0.3 to about 2 parts of said photoinitiator and/or photosensitizer, all based on 100 parts by weight of said urethane prepolymer.

20 8. A foam composition comprising the resin of claim 1.

9. A foam composition comprising the resin of claim 3.

10. A laminate comprising a layer of the foam composition of claim 8 wherein said foam composition has a  
25 thickness of between about 10 to about 150 mils.

11. A laminate comprising a layer of the foam composition of claim 9 wherein said foam composition has a thickness of between about 10 to about 150 mils.

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12. A foam sheet comprising the foam composition of claim 8 wherein said foam sheet has a thickness of between about 10 to about 150 mils.

13. The foam sheet of claim 12 further comprising  
5 a built-in support material.

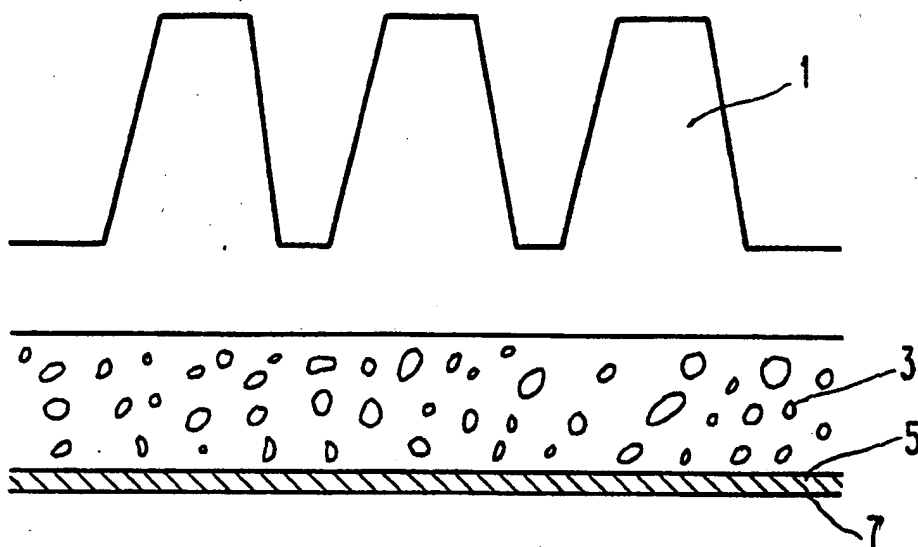
14. The foam sheet of claim 13 wherein said support material is a mesh-like material having a thickness of between about 1 to about 20 mils.

15 15. A printing blanket comprising the foam composition of claim 8 wherein said foam composition has a thickness of between about 10 to about 150 mils.

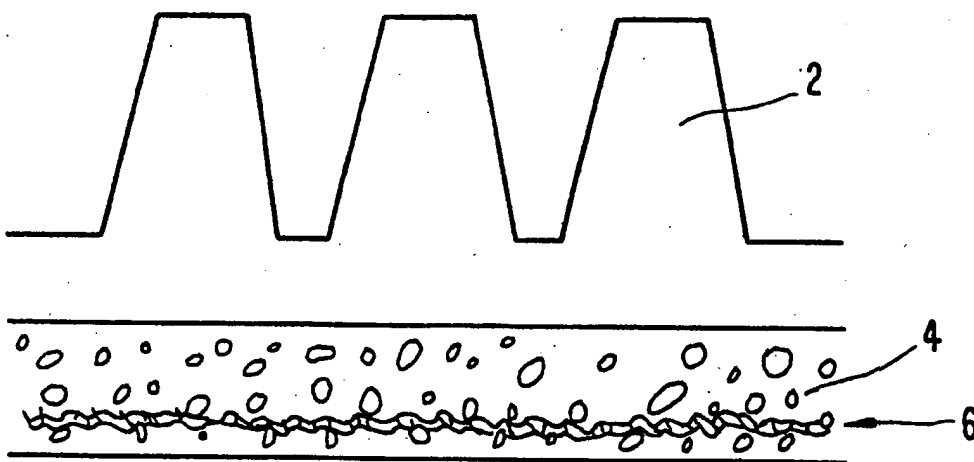
16. A printing blanket comprising the foam composition of claim 10 wherein said foam composition has a thickness of between about 10 to about 150 mils.

15 17. A compressible printing plate comprising the foam composition of claim 8 wherein said foam composition has a thickness of between about 10 to about 150 mils.

18. A compressible printing plate comprising the foam composition of claim 10 wherein said foam composition  
20 has a thickness of between about 10 to about 150 mils.



***Fig. 1***



***Fig. 2***



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/00963

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.  
US CL : 522/90, 96, 97; 428/160, 411.1, 245, 304.4; 101/453.  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 522/90, 96, 97; 428/160, 411.1, 245, 304.4; 101/453.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: THIOL, POLYTHIOL, (METH)ACRYLATED POLYURETHANE, FOAM OR FROTH, GRAPHIC ARTS, PRINTING PLATE, PRINTING BLANKET, LAMINATE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,535,193 (PRINCE) 20 October 1970, column 2, lines 6-35, column 3, lines 24-26, column 4, lines 25-38, column 5, lines 7-17, 28-31, 43-47.	1-18
Y	US, A, 4,771,078 (SCHISLER ET AL) 13 September 1988, Abstract, column 2, lines 3-26, 53-63, column 3, lines 30-61, column 6, line 57, to column 8, line 66, column 9, lines 16-34.	1-18
Y	US, A, 4,241,131 (BAILEY) 23 December 1980, Abstract, column 2, lines 5-45, column 10, line 62, to column 11, line 12.	1-14

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 MAY 1996

Date of mailing of the international search report

21 MAY 1996

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/00963

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,120,721 (KETLEY ET AL) 17 October 1978, column 1, line 6, to column 4, line 65, column 5, lines 10-37, column 6, lines 47-62, column 7, line 57, to column 8, line 28.	1-18
Y	US, A, 4,582,777 (FISCHER ET AL) 15 April 1986, column 1, line 54, to column 2, line 17.	1-18
Y	US, A, 4,008,341 (KEHR) 15 February 1977, Abstract, column 2, lines 21-63, column 3, lines 4-14, column 3, line 66, to column 4, line 10, Examples 18-19, column 18, lines 53-66.	1-18
Y	US, A, 4,481,281 (TSAO ET AL) 06 November 1984, column 5, lines 4-54, Examples III and IV.	1-18

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/00963

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/00963

## A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

B41N 1/00, 3/00, 3/03, 3/04, 3/08; B32B 3/12, 3/26, 7/00, 9/04; C08L 75/00, 75/16.

## BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-9, drawn to a composition and a foam product comprising the composition, classified in Class 428, subclass 160.

Group II, claims 10-11, drawn to a foam sheet comprising the foam composition on a substrate, classified in Class 428, subclass 411.1.

Group III, claims 12-14, drawn to a foam sheet comprising the foam composition and a built-in support material, classified in Class 428, subclass 245.

Group IV, claims 15-16, drawn to a printing blanket comprising the foam composition, classified in Class 428, subclass 304.4.

Group V, claims 17-18, drawn to a compressible printing plate comprising the foam composition, classified in Class 101, subclass 453.

The inventions listed as Groups I-V do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reason. Although each of the products recited in claims 10-18 comprise the foam composition recited in claims 8-9, the foam composition is not considered to be a special technical feature therein since it is admitted at page 1 of the description under "Background of the Invention" that the use of foam sheets in these industries is "well known in the art". Applicant has not shown that the particular foam composition gives some unexpected results to the foam sheets, printing blanket or printing plate.